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Effect of Aliphatic Mono Carboxylic acids and alcohols on Silver (I) Catalyzed oxidation of SO_2 in aqueous solution

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Abstract

In this paper we report the comparative study of formic acid and isopropyl alcohol on SO_2 oxidation in pH range 4.02-5.25 in the presence of silver (I). Based on the observed results following rate law given and a free radical mechanism has been proposed:

$$-d[S(lV)]/dt \quad = \quad (k_1 + k_2[Ag(I)])\,[S(lV)]/1 + B\,[Organics]$$

Experiments were carried out at $30 \le T°C \le 40$, $4.02 \le pH \le 5.25$, 1×10^{-3} mol/dm^3 $\le [S(lV) \le 10\times10^{-3}$ mol/dm^3, 5×10^{-6} mol/dm^3 $\le [Ag(I)] \le 2.5\times10^{-5}$ mol/dm^3, 5×10^{-6} mol/dm^3 $\le$ [Formic acid] $\le 8\times10^{-4}$ mol/dm^3, 5×10^{-7} mol/dm^3 $\le$ [Isopropyl alcohol] $\le 8\times10^{-4}$ mol/dm^3. Rate constants and order of reaction were calculated and found pseudo- first order in all cases. The effect of pH and temperature were also discussed. The value of apparent energy were found as 79.3 kJ mol^{-1} and 79.83 kJ mol^{-1}in the presence of formic acid and isopropyl alcohol respectively.

1. Introduction

A large number of organic and inorganic chemical species are released into the atmosphere by anthropogenic and natural sources. The atmospheric reactions of SO_2 and NO_x etc. are major acid rainprecursors and are responsible for acidification of various forms of atmospheric water. Studies in India and abroad have shown that anthropogenic sources in the atmosphere are the major contributors of SO_2 and NO_x which are transformed in to acids such as HNO_2, HNO_3, H_2SO_3 and H_2SO_4 (Berresheim and Jaeschke *et al.*[1].Measurable quantities of low molecular weight (LMW) aldehydes and monocarboxylic acids are present in Los angeles urban atmospheres (Grosjean[2], Kawamura *et al.*[3], and rural/remote atmosphere (Keene *et al.* [4], Khwajaet[5], Talbot *et al.*[6], ,Helas*et al.* [7]. Studies of rainwater composition showed that C_1–C_{10} monocarboxylic acids, C_2–C_{10}dicarboxylic acids and C_1–C_2 aldehydes are present in wet precipitation as major organic species (Kawamura *et al* [8].The compounds primarily originate from incomplete combustion of fossil fuels mainly by automobiles and secondarily from photochemical reactions of anthropogenic hydrocarbons and other precursors in the atmosphere (Kawamura *et al.*, 1985b[9],Chebbi and Carlier, 1996[10], Kawamura *et al.*, 2000[11]).Alcohols commonly present both in urban and in rural atmosphere add to the group of pollutants termed volatile organic compounds (VOCs) reported by (J. Ziajka, W. Pasiuk-Bronikowska 2003)[12]. Bigelow (1898)[13], was the first who found experimentally that alcohols, such as methanol, ethanol, propanol and butanol, slow down the reaction between sodium sulphite and air oxygen. His aim was to gain some quantitative data to widen the knowledge on catalysis. The inhibiting effect of aliphatic alcohols (ethanol, isopropanol, secondary butanol and benzyl alcohol) on the oxidation of sodium sulphite was then investigated by Alyea and Backstrom (1929)[14], in a chain reaction theory-based study. The methanol inhibition of the uncatalysed autoxidation of HSO_3 was investigated by Connick*et al.*(1995)[15], to shed more light on a mechanism of initiation in the absence of transition metal ions. Sharma *et al.* studied the inhibiting effect of formic acid(2015)[16], isopropyl alcohol, (2016)[17], in the presence of silver (I) catalyzed autoxidation of SO_2 and report that both are influence the SO_2 oxidation in the atmosphere with moderate rates. Since in this paper we present the comparison of both compounds to know better inhibitor for SO_2 oxidation in acidic medium insilver (I) catalyzed reaction.

2. Material and Methods

The experimental procedure was exactly the same as described earlier [18]. All the chemicals used AR grade. And their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at an outer part for circulating thermostatic water for maintaining the desired temperature $30\underline{+}1^0$C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at $1600\underline{+}10$ rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreached S(IV) iodometrically. The reproducibility of replicate measurements was generally better than $10\underline{+}1$ %. All calculations were performed in MS Excel. The schematic diagram of the experimental set up for the kinetic study of $SO_2 – O_2$ oxidation reaction is given in figure.1

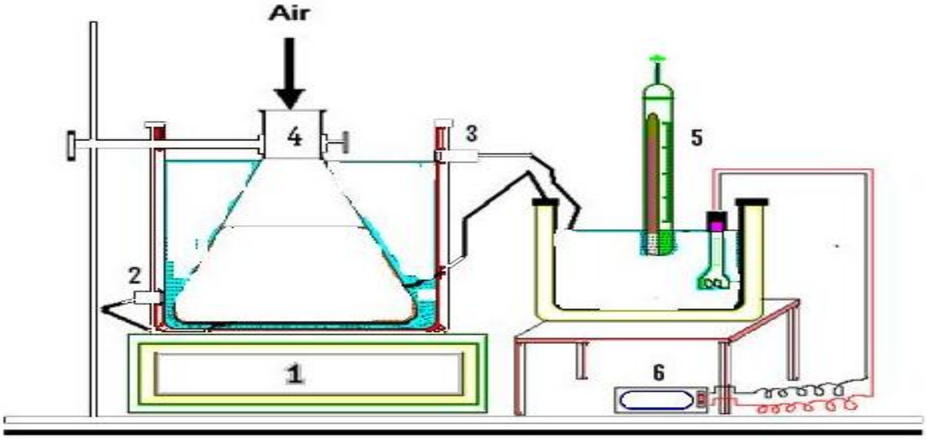

Figure 1:. 1. Magnetic Stirrer, 2. Water Inlet, 3.Water outlet, 4.Erlenmeyer flask (Reaction mixture), 5.Thermometer, 6.Thermostat.

3. **Results and Discussion**

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S (VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure . The product analysis showed the recovery of sulphate to be $98\underline{+}1$%., in all cases in agreement with eq. (1)

$$S(IV) + 0.5\,O_2 \longrightarrow S(VI). \qquad (1)$$

3.2 Preliminary Investigation

The kinetics of both uncatalysed and silver (I) catalyzed, formic acid and isopropyl alcohol inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30 ^oC. In all the cases the pseudo first orderdependence of sulfur (IV) was observed in the kinetics data treatment for the determination of pseudo first orderrate constant $k_1$was calculated from *log [S(IV)]* versus time, *t*. The plots were shown in figure 2. From the figure 2 it is observed that both the uncatalysed and silver (I) catalyzed autoxidation of sulfur (IV) reaction are inhibited by formic acid and isopropyl alcohol.

3.3 Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of silver (I) and all the solutions were prepared in doubly distilled water.

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30 ^oC in acetate buffered medium. The kinetics was found to be pseudo first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of pseudo first order rate constant k_1 are given in Table- 1 The dependence of reaction rate on [S(IV)] follows the rate law (2)

$$-d\,[S(IV)]\,/dt = k_1\,[S(IV)]. \qquad (2)$$

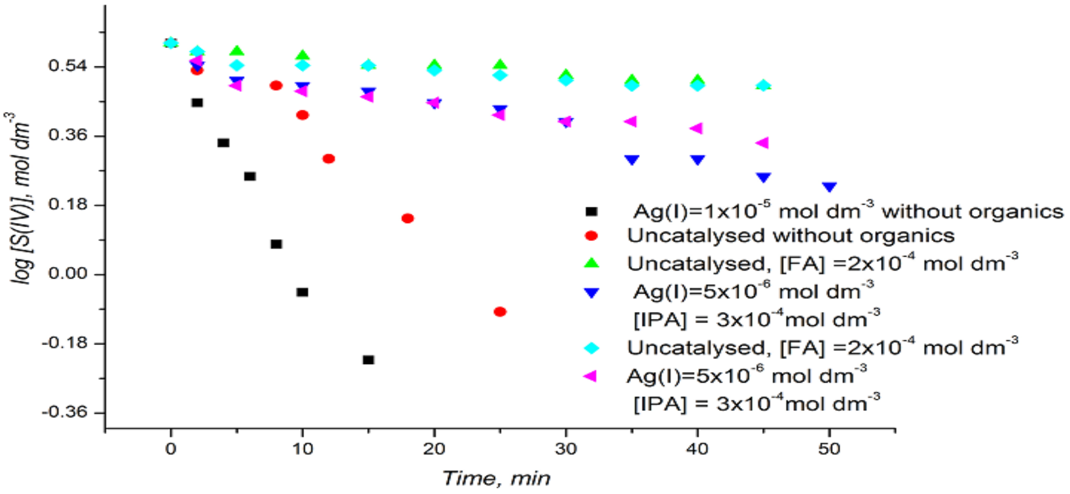

Figure 2: The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30 ^{o}C with uncatalysed, silver (I) catalyzed, formic acid and isopropyl alcohol inhibited reaction.

Table 1: The values of k_1 for uncatalysed reaction at different [S(IV)] at pH = 4.95, t = 30 ^{o}C $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	**(10^{3}) k_1 s^{-1}**
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

3.5 [Organics] Dependence

The major aim of this study was to examine the effect of formic acid and isopropyl alcohol on the autoxidation of S(IV) in acetate buffer medium and varying the [Organics] from $5x10^{-7}$ mol dm^{-3} to $8x10^{-4}$ mol dm^{-3} we observed the rate of thereaction decreased by increasing [Organics] The results are given in Table 2 However the nature of the [S(IV)] dependence in presence of organics did not change and remains pseudo first order. The pseudo first order at constant k_{inh}, in the presence of organics was defined by rate law (3):

$$-d\left[S\ IV\right]/dt = k_{inh}\left[S\ IV\right]. \qquad (3)$$

The values of k_{inh}in the presence of organics decreased with increasing [Organics] are given in Table 2 which are in agreement with the rate law (4):

$$k_{inh} = k_1 / (1+B\,[organics]) \qquad (4)$$

Where B is inhibition parameter for rate inhibition by organics
The equation (4) on rearrangement becomes:

$$1/ k_{inh} = 1/ k_1 + B\,[organics] / k_1 . \qquad (5)$$

In accordance with the equation (5) the plot of $1/ k_{FA}$ v/s [Formic acid] was found to be linear with non- zero intercept. The values of intercept ($1/ k_1$) and slope (B/ k_1) were found to be $3.03x10^{7}$ mol dm^{-3}s and $9.1x10^{2}$ s at pH = 4.95, t = 30 ^{o}C. From these values the value of inhibition parameter B was found to be **$3.33x10^{4}$ mol dm^{-3}**Similarly the plot of $1/ k_{IPA}$ v/s [Isopropyl alcohol] was found to be linear with non- zero intercept. The values of intercept ($1/ k_1$) and slope (B/ k_1) were found to be 1.11 x 10^4 s and 5.47 x 10^6 mol dm^{-3}s at pH = 4.95, t = 30 ^{o}C. From these values the value of inhibition parameter B was found to be **4.92 x 10^{3} mol dm^{-3}**

Table 2: The values of k_{inh} at different [Organics] at pH = 4.95, t = 30 °C $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	**$10\ ^{3}k_{FA}$ s^{-1}**	**$1/k_{FA}$ s**	**[Isopropyl alcohol] mol dm^{-3}**	**$10\ ^{3}k_{IPA}$ s^{-1}**	**$1/k_{IPA}$ s**
0.0	1.09	917	0.0	1.09	917
$5.0x10^{-6}$	0.98	1020	$5.0x10^{-7}$	1.17	855
$8.0x10^{-6}$	0.76	1316	$8.0x10^{-7}$	1.1.3	885
$1.0x10^{-5}$	0.57	1754	$3.0x10^{-6}$	1.08	926
$3.5x10^{-5}$	0.38	2632	$5.0x10^{-6}$	0.93	1075
$7.5x10^{-5}$	0.26	3846	$1.0x10^{-5}$	0.80	1250
$1.0x10^{-4}$	0.19	5263	$5.0x10^{-5}$	0.77	1299
$3.0x10^{-4}$	0.15	6667	$7.0x10^{-5}$	0.48	2083
$5.0x10^{-4}$	0.07	14286	$3.0x10^{-4}$	0.38	2632
$8.0x10^{-4}$	0.03	33333	$8.0x10^{-4}$	0.18	5556

3.6 Ag(I) Catalyzed Reaction

At first the kinetics of Ag(I) Catalyzed reaction in the absence of inhibitor was studied.

3.7 [S(IV)] Variation

The dependence of sulfur (IV) on reaction rate was studied by varying [S(IV)] from $1x10^{-3}$ mol dm^{-3} to $10x10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5x10^{-6}$ mol $dm^{-3}$and $1x10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30 ° The kinetics was found to be pseudo first order in [S(IV)] v/s time were linear as shown in Figure 2.

3.8 Ag(I) variations

The dependence of Ag(I) on the reaction rate was studied by varying silver (I)from $5x10^{-6}$ mol dm^{-3} to $2.5x10^{-5}$ mol dm^{-3} at S(IV) = $2x10^{-3}$ mol dm^{-3} pH= 4.95, t= 30 ° C in acetate buffer medium. The values of pseudo first order rate constant k_{cat} for S(IV) oxidation was determine are shown in figure 3. Similarly the effect of catalyst in presence of both inhibitors shown in figure 4. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law (6)

$$-d [S(IV)] /dt = k_{cat} [SIV)] = (k_1+k_2[Ag(I)] [S(IV)] \quad (6)$$

$$k_{cat} = k_1+k_2 [Ag(I)]. \quad (7)$$

From the plot in figure 3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 0.72x 10^{1} s and 8.6 x 10^{-3} mol dm^{-3} srespectively at pH = 4.5, t = 30 °C, in acetate buffered medium.

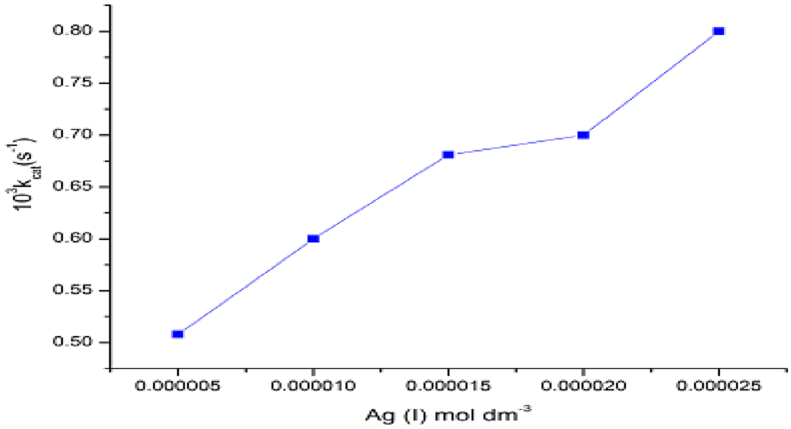

Figure3: The dependence of catalyst concentration at [S(IV)] = $2x10^{-3}$ mol dm^{-3} pH = 4.95, t = 30 °C, in acetate buffered medium.

3.9 Variation of pH

Variation of pH was carried out from 4.02- 5.25 at different [S(IV)], silver (I), [Formic acid], [Isopropyl alcohol] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. From the plot of log k_1 v/s log (H^+). The order with respect to H^+ is 0.20 which is a fractional order and can be neglected as shown in **Table 3**

Table 3: Rate of silver(I) catalyzed autoxidation in the presence of Formic acid and Isopropyl alcohol.

[Formic acid], mol dm^{-3}	**silver (I) =5x10^{-6} mol dm^{-3}**	**[Isopropyl alcohol], mol dm^{-3}**	**silver (I) =5 x 10^{-6} mol dm^{-3}**
pH = 4.02			
7.5 x 10 $^{-5}$	0.253 x 10^{-3}	7.0 x 10 $^{-5}$	0.401 x 10^{-3}
1.0 x 10^{-4}	0.055 x 10^{-3}	3.0 x 10^{-4}	0.264 x 10^{-3}
3.0 x 10^{-4}	0.047 x 10^{-3}	8.0 x 10^{-4}	0.170 x 10^{-3}
pH = 4.5			
7.5 x 10 $^{-5}$	0.426 x 10^{-3}	7.0 x 10 $^{-5}$	0.611 x 10^{-3}
1.0 x 10^{-4}	0.299 x 10^{-3}	3.0 x 10^{-4}	0.407 x 10^{-3}
3 .0x 10^{-4}	0.267 x 10^{-3}	8.0 x 10^{-4}	0.337 x 10^{-3}
pH = 5.25			
7.5 x 10 $^{-5}$	0.553 x 10^{-3}	7.0 x 10 $^{-5}$	0.925 x 10^{-3}
1.0 x 10^{-4}	0.425 x 10^{-3}	3.0 x 10^{-4}	0.582 x 10^{-3}
3.0 x 10^{-4}	0.408 x 10^{-3}	8.0 x 10^{-4}	0.430 x 10^{-3}

3.10 [Organics] Dependence

To know the effect of formic acid and isopropyl alcohol on silver (I) catalyzed autoxidation of S(IV), formic acid variation was carried out from 5x10^{-6} mol dm^{-3} to 3 x 10^{-4} mol dm^{-3} isopropyl alcohol variation was from 5x10^{-7} mol dm^{-3} to 8 x 10^{-4} mol dm^{-3} at two different silver (I) that is 5x10^{-6} mol dm^{-3} to 1 x 10^{-5} mol dm^{-3} but fixed sulfur (IV) = 2x10^{-3} mol dm^{-3} at pH= 4.95 and temp 30 ^{o} C. The results indicated that by increasing organics the rate becomes decelerates.

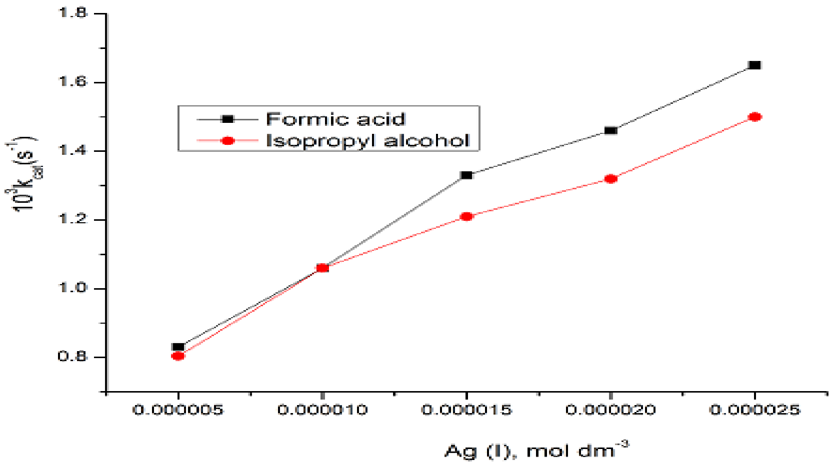

Figure 4: Effect of catalyst at [S(IV)] = 2x10^{-3} mol dm^{-3} (Formic acid)= 7.5x10^{-5} mol dm^{-3}, [Isoproyl alcohol]= 7.0x10^{-5} mol dm^{-3} pH= 4.95 t= 30 ^{o}C in acetate buffered medium.

Figure 5 shows depending on the observed results the reaction follows the following rate law (8)

$$-d\left[S\ IV\right]/dt = (k_1+k_2\left[Ag\ I\quad S\ IV\right] / 1 + B\ \ organics \tag{8}$$

$$\text{Where } k_{inh} = (k_1+k_2[Ag(I)] / 1 + B\,[organics] = k_{cat} / 1 + B\,[organics]\,, \tag{9}$$

$$1/\ k_{inh} = 1 + B\,[organics]\ / k_{cat}\,, \tag{10}$$

$$1/\ k_{inh} = 1/ k_{cat} + B\,[organics] / k_{cat}\,. \tag{11}$$

3.11 Effect of temperature

The values of k_{obs} were determined at three different temperatures in the range of 30 ^{o}C to 40 ^{o}C. The results are given in Table 4. By plotting a graph between *log k v/s 1/t* yield us an apparent empirical energy of activation 79.3 kJ mol^{-1} and 71.83 kJ mol^{-1} in the presence of formic acid and isopropyl alcohol respectively.

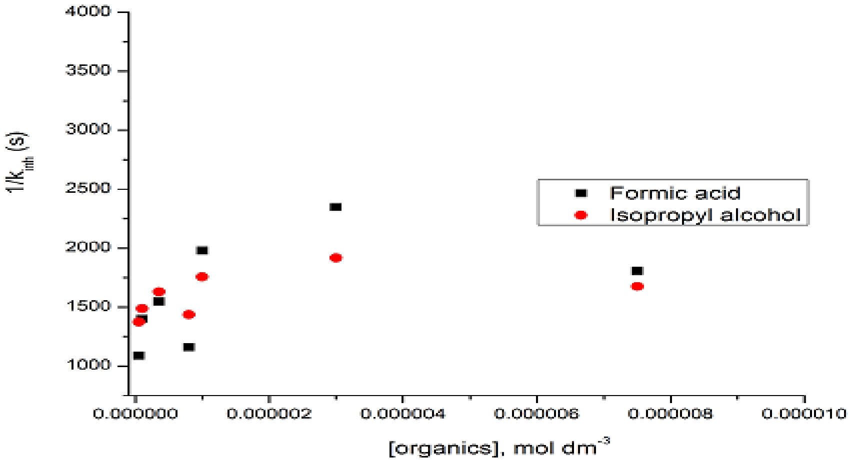

Figure 5: Effect of organics at [S(IV)] = 2x10^{-3} mol dm^{-3} silver (I) = 5x10^{-6} mol dm^{-3} pH = 4.95, t = 30 °C, in acetate buffered medium. From this graph the value of B_{FA} and B_{IPA} are found as 2.53 x 10^{3} mol dm^{-3} and 2.03 x10^{3}mol dm^{-3} respectively.

Table 4: Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = 2x10^{-3} mol dm^{-3} at silver (I) = 5 x10^{-6} mol dm^{-3} [Formic acid] = 7.5 x 10 $^{-5}$ mol dm^{-3} [Isoproyl alcohol]= 7.0x10^{-5} mol dm^{-3} pH = 4.95.

t °C	**10 ^{3} k_{FA} s^{-1}**	**10 ^{3} k_{IPA} s^{-1}**
30	0.42	0.88
35	0.62	1.13
40	0.74	1.73

3.12 Discussion

SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH = 4.05-5.25 the following equilibrium operates in eq. 12

$$HSO_3^{-1} \rightleftharpoons H^{+} + SO_3^{-2}. \qquad (12)$$

In this range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. The order of reaction was 0.20 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz, (2008)[19]. Gupta *et al.* (2012), [20] studied that ammonia which is present in atmospheric water in trace amount are also contribute in inhibition of SO_2.Q.Li*et al.*(2014, 2017), [21-22] studied the magnesium sulphite oxidation by cobalt ions and multiwalled carbon nanotubes and reported that both are promoted the oxidation reaction. L. Wang *et al.*(2013, 2015,2016), [23-25] studied the magnesium sulphite oxidation by ascorbic acid, transition metal catalyst, cobalt based molecular sieve and found ascorbic acid inhibited the reaction, transition metal catalysts is promoting the oxidation of solid sulfites influe gas desulfurization and magnesium sulphite oxidation is promoted by a novel cobalt-based molecularsieve catalyst respectively. The rate of uncatalysed and silver (I) catalyzed reaction is decelerated by the addition of Formic acid and Isopropyl alcohol in the present study. Manoj*et al.* (2008)[26] Sameena *et al.* (2013)[27] Sharma *et al.* (2017) [28-30] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^{3} - 10^{4} In the present study the value of inhibition parameter for uncatalysed and silver (I) catalyzed autoxidation of sulfur (IV) by formic acid and isopropyl alcohol are found to be in the range. This is strongly support the radical mechanism in the present case too based on the observed results.

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \qquad K_d = 5.01 \times 10^{-7} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \qquad K_{oAc} = 2.29 \qquad (14)$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \qquad K_1 = 2.51 \times 10^5 \qquad (15)$$

$$Ag^+ + HSO_3^{-1} \overset{k_2}{\rightleftharpoons} AgHSO_3 \qquad (16)$$

$$AgOSO_2^- + O_2 \overset{K_3}{\rightleftharpoons} AgOSO_2^{-1}.O_2 \qquad (17)$$

$$AgHSO_3 + O_2 \overset{K_4}{\rightleftharpoons} AgHSO_3.O_2 \qquad (18)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (20)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (21)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (22)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (23)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (24)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (25)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (26)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (27)$$

$$SO_4^{-\bullet} + \text{organics} \xrightarrow{k_{10}} \text{Non Chain product .} \qquad (28)$$

By assuming long chain hypothesis and steady state approximation d[$SO_3^{-\bullet}$]/dt, d[$SO_4^{-\bullet}$]/dt, d[$SO_5^{-\bullet}$]/dt, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 29)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[organics]\}\ [SO_4^{-1}]. \qquad (29)$$

Since the reaction is completely stopped in the presence of [Organics] = 8x10^{-4} mol dm^{-3}, so the step (22) and (25) appear to be unimportant. The step (24) is ignored because the reaction is completely seized in the presence of higher concentration of organics by omission and substitution from the above mechanism the following rate law can be obtain (30)

$$R_{cat} = k_1\ [Ag(I)]\ [S(IV)]\ /\ \{k_9[x] + k_{10}[organics]\}\ . \qquad (30)$$

By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 2.53 x 10 ^{3} mol dm^{-3} and 2.03 x 10 ^{3} mol dm^{-3} by formic acid and isopropyl alcohol respectively which is in the range of 10^3 -10^4 and also coincide with the reported value of B of Co_2O_3catalysed autoxidation of S(IV) by formic acid is 3.58 x 10 ^{3} mol dm^{-3} So on the basis of calculated value of B we concluded that organics act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

Conclusions

The role of organics act as an inhibitor in Ag(I) catalysed autoxidation of SO_2 in acidic medium has been find, and based on the observed results rate law a free radical mechanism has been proposed.

$-d[(SIV)/dt = (k_1+k_2[Ag])[(SIV)]/1 + B[organics]$ Rate law

$R_{cat} = k_1 [Ag(I)][S(IV)] / \{k_9[x] + k_{10}[organics]\}$.

Based on the experimental results, rate constants and order of the reactions were determined. The reaction order in $SO_2$was pseudo first order for both reactions in the presence and absence of organics. The effect of pH on SO_2 oxidation in the presence of Ag(I) and organics has been studied and found rate of the SO_2 oxidation depends on the initial pH of the solution but it is independent of the pH change during the reaction. The effect of temperature of solution on SO_2 oxidation catalysed by Ag(I) in presence of organics were discussed. By plotting a graph between *log k* v/s *1/T* yield gives us an apparent empirical energy of activation which is found 79.3 kJ mol^{-1} for formic acid and 71.83 kJ mol^{-1} for isopropyl alcohol respectively. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of SO_2 in the presence of *formic acid and isopropyl alcohol* study here found $2.53x10^3$ mol dm^{-3} and $2.03x10^3$ mol dm^{-3} which is confirm that formic acid is best inhibitor compare to isopropyl alcohol which is also coincide by E_a higher for formic acid than isopropyl alcohol.Organics are able to inhibit the oxidation of SO_2 so rain water acidity can be controlled.They increase the life span of SO_2 so vegetation, national buildings, monuments, fishes of water bodies and human being are not affected by rain water acidity.The results are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry. This study is important in understanding the mechanism of the atmospheric oxidation of S(IV) by O_2

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